CLAIMS

1) Process for oxidative desulphurization of hydrotreated hydrocarbon mixtures which boil within the range of 180° to 360°C, containing less than 350 ppm of sulphur as thiophenic compounds, which comprises:

a) putting these mixtures in contact, in the presence of an organic peroxide, with a catalytic composition comprising a completely amorphous micro and/or mesoporous mixed oxide containing an oxide matrix selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or more oxidative metal oxides selected from transition metal oxides and group IVA metal oxides are uniformly dispersed, and

b) separating the obtained corresponding sulphur oxygenated products from the hydrocarbon mixture.

2) Process according to claim 1, wherein the surface of the catalytic composition has $-O-Si(R)_3$ groups, R being the same or different each other and being selected from C_1-C_4 alkyl, aryl and polyaryl groups, that optionally contain functional groups selected from acids, amines, thiols, sulfonics or trialkylamines.

3) Process according to claim 1 or 2 wherein the oxidative dispersed metal oxide is selected from oxide of Ti, V, Zr, Sn and there mixtures.

4) Process according to claim 1 or 2 wherein the catalytic composition contains boron and/or gallium oxides.

5) Process according to claim 1 wherein the molar ratio in catalytic composition between the oxide matrix (YO) selected from silica, alumina, ceria, magnesia and mixtures of thereof, and the dispersed metal oxide (MO) is between 5/1 and 300/1.

6) Process according to claim 5 wherein the molar ratio in catalytic composition between the oxide matrix (YO) and the dispersed metal oxide (MO) is between 10/1 and 200/1.

7) Process according to claim 4 wherein the molar ratio in catalytic composition between the oxide matrix (YO) and the boron or/and gallium oxides is between 5/1 and 300/1.

8) Process according to claim 1 or 2 wherein in the catalytic composition the oxide matrix is selected from silica, alumina and mixture thereof, and the metal oxide is selected from the oxides of titanium, zirconium, vanadium, tin.

9) Process according to claim 8 wherein the metal oxide is oxide of titanium.

10) Process according to claim 1 or 2 wherein the catalytic composition is a completely amorphous micro-mesoporous mixed oxide characterized by a surface area of more than 500 m^2/g, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å.

11) Process according to claim 10 wherein the catalytic composition is a completely amorphous micro-mesoporous mixed oxides of MSA type whose XRD spectrum from powders does not have a crystalline structure and does not show any peak.

12) Process according to claim 10 wherein the catalytic composition is a completely amorphous micro-mesoporous mixed oxide of ERS-8 type whose XRD spectrum from powders does not have a crystalline structure, does not show any peak and shows a widespread scattering at angular value not greater than $2\theta = 5°$, with CuKα radiation, while other scattering phenomena coherent for greater angular values are absent.

13) Process according to claim 11 wherein the catalytic composition is a completely amorphous micro-mesoporous mixed oxide consisting of a silica or a silica and alumina matrix wherein one or more metal oxide are uniformly dispersed, these being selected from the oxides of titanium, zirconium, vanadium, tin,

characterized by a surface area of more than 500 m^2/g, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å.

14) Process according to claim 12 wherein the catalytic composition is a completely amorphous micro-mesoporous mixed oxides consisting of a matrix of silica or a matrix of silica and alumina, wherein one or more metal oxides are uniformly dispersed selected from oxides of titanium, zinc, vanadium and tin, characterized by a surface area of more than 500 m^2/g, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å.

15) Process according to claim 2 wherein in the catalytic composition the molar ratio between the metal oxide matrix and the dispersed metal oxide is higher than 5 and less or equal to 400.

16) Process according to claim 1 o 2 wherein the catalytic composition is used as such or extruded using a binder and a peptizing agent added to the catalyst to produce an estrudable paste.

17) Process according to claim 1 or 2 wherein the organic peroxide is an alkyl- or an aryl-hydroperoxide, or a dialkyl- or diaryl-peroxide, wherein the alkyl or aryl groups are the same or different.

18) Process according to claim 17 wherein the organic peroxide is terbutyl hydroperoxide or cumyl hydroperoxide.

19) Process according to claim 1 or 2 carried out at a temperature ranging from 50 to 120°C.

20) Process according to claim 1 or 2 carried out in the presence of an organic peroxide with a molar ratio in respect to S lower than or equal to 30.

21) Process according to claim 20 carried out in presence of an organic peroxide with a molar ratio in respect to S ranging from 2 to 30.

22) Process according to claim 21 wherein the organic peroxide is in a molar ratio in respect to S ranging from 2 to 14.

23) Process according to claim 1 or 2 carried out at a temperature ranging from 50 to 120°C, in presence of an organic peroxide with a weight ratio in respect to S ranging from 2 to 15.

24) Process according to claim 19 or 23 carried out at a temperature ranging from 60 to 90°C.

25) Process according to claim 1, 2 or 23 carried out at atmospheric pressure.

26) Process according to claim 1 or 2 wherein the hydrotreated hydrocarbon mixture is LCO.

27) Process according to claim 1 or 2 carried out in unique organic phase and in absence of added solvent.

28) Process according to claim 1 or 2 wherein the separation of the obtained sulphur oxygenated products from the hydrotreated hydrocarbon mixtures is carried out by distillation, by solvent extraction methods or by selective adsorption.

29) Process according to claim 28 wherein the solvent extraction methods are carried by extraction with methanol, acetonitrile, dioxane, methyl-terbutyl-ether.

30) Process according to anyone of the preceding claims wherein the mixed oxide comprises silica and alumina in the molar ratio $SiO_2/Al_2O_3 \geq 30$.

31) Catalytic composition comprising a completely amorphous micro-mesoporous mixed oxide consisting of a silica and alumina matrix wherein one or more metal oxides are uniformly dispersed, these being selected from the oxides of titanium, zirconium, vanadium, tin, characterized by a surface area of more than 500 m^2/g, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å, and a XRD spectrum

from powders that does not have a crystalline structure and does not show any peak.

32) Catalytic composition comprising a completely amorphous micro-mesoporous mixed oxide consisting of a matrix of silica or a matrix of silica and alumina, wherein one or more metal oxides are uniformly dispersed selected from oxides of titanium, zinc, vanadium and tin, excluding the mixed oxides containing a silica matrix wherein titanium oxide is uniformly dispersed, said catalytic composition being characterized by an X-ray diffraction spectrum (XRD) that does not have a crystalline structure, has a widespread reflection at angular value not greater than $2\theta = 5°$, with CuKα radiation, while other scattering phenomena coherent for greater angular values are absent.

33) Catalytic composition comprising a completely amorphous micro-mesoporous mixed oxide containing an oxide matrix selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or more metal oxides selected from oxides of Ti, V, Zr, Sn, are uniformly dispersed, excluding the mixed oxide of MSA type containing a silica matrix wherein one or more metal oxides are uniformly dispersed selected from the

oxides of titanium, zirconium, vanadium, tin and excluding the mixed oxide of ERS-8 type containing a silica matrix wherein titanium oxide is uniformly dispersed.

34) Catalytic composition comprising a completely amorphous micro and/or mesoporous mixed oxides containing a matrix selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or more metal oxides selected from transition metal oxides and group IVA metal oxides are uniformly dispersed, whose surface has $-O-Si(R)_3$ groups, R being the same or different each other and being selected from C_1-C_4 alkyl, aryl and polyaryl groups, that optionally contain functional groups selected from acids, amines, thiols, sulfonics or trialkylamines.

35) Catalytic composition according to claim 34 wherein the oxidative dispersed metal oxide is selected from oxide of Ti, V, Zr, Sn and their mixtures.

36) Catalytic composition according to claim 31, 32, 33 or 34 wherein the mixed oxide contains silica and alumina in the molar ratio SiO_2/Al_2O_3 is $\geq$ 30.

37) Catalytic composition according to claim 31, 32, 33 or 34 wherein the catalytic composition contain boron and/or gallium oxides.

38) Catalytic composition according to claim 34 wherein the molar ratio in catalytic composition between the oxide matrix and the oxidative dispersed metal oxide is higher than 5 and less or equal to 400.

39) Catalytic composition according to claim 34 wherein in the catalytic composition the metal oxide matrix is selected from silica, alumina and mixture thereof, and the metal oxide is selected from the oxides of titanium, zirconium, vanadium, tin.

40) Catalytic composition according to claim 39 wherein the metal oxide is oxide of titanium.

41) Catalytic composition according to claim 34 comprising a completely amorphous micro-mesoporous mixed oxide characterized by a surface area of more than 500 m^2/g, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å, whose XRD spectrum from powders does not have a crystalline structure and does not show any peak.

42) Catalytic composition according to claim 34 comprising a completely amorphous micro-mesoporous mixed oxide characterized by a surface area of more

than 500 m^2/g, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å, whose XRD spectrum from powders does not have a crystalline structure, does not show any peak and shows a widespread scattering at angular value not greater than $2\theta = 5°$, with CuKα radiation, while other scattering phenomena coherent for greater angular values are absent.

43) Process for preparing the catalytic composition of claim 41 comprising a completely amorphous micro-mesoporous mixed oxides containing a matrix selected from silica, alumina, ceria, magnesia and mixtures of thereof (YO), wherein one or more metal oxides (MO) selected from transition metal oxides and group IVA metal oxides are uniformly dispersed, whose surface has $-O-Si(R)_3$ groups, R being the same or different each other and being selected from C_1-C_4 alkyl, aryl and polyaryl groups, that optionally contain functional groups selected from acids, amines, thiols, sulfonics or trialkylamines, characterized by a surface area of more than 500 m^2/g, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å, whose XRD spectrum from powders does not have a

crystalline structure and does not show any peak, said process comprising:

(a) subjecting to hydrolysis and gelification a solution of one or more soluble or hydrolizable compounds of Si, Al, Ce, Mg, or mixture thereof, in alcohol, with an aqueous solution of a hydroxide of tetra-alkylammonium having the formula (I):

$$R'_4N\text{-}OH$$

wherein R' represents a C_3-C_7 alkyl group and of one or more soluble or hydrolizable compounds of one or more metals selected from Ti, V, Zr, Sn, the quantity of the constituents of the above solution being such as to respect the following molar ratios:

alcohol/YO = 5-20

R'_4N-OH/YO = 0.05-0.5;

H_2O/YO = 5-30

YO/MO $\geq$ 5

whereas the ratio H2O/R'_4N^+ varies according to the number of carbon atoms in the R' alkyl chain , in accordance with the values shown in table A below :

Table A

R'	H_2O/R'_4N+
Hexyl	> 133
Pentyl	> 100

Butyl	> 73
Propyl	> 53

operating at a temperature close to the boiling point, at atmospheric pressure, of the alcohol used and of any alcohol which develops as by-product of the above hydrolysis reaction, without the elimination or substantial elimination of said alcohols from the reaction environment, preferably at a temperature of between 20°C and 80°C;

(b) subjecting the gel obtained in step (a) to drying;

(c) outgassing the obtained material in vacuum and then adding a solution of silylating agent in solvent;

(d) refluxing the resulting mixture under inert atmosphere and then filtering the obtained product, washing and subjecting it to drying.

44) Process for preparing the catalytic composition of claim 43 comprising :

(a) subjecting to hydrolysis and gelification a solution of one or more soluble or hydrolizable compounds of Si and Al, in alcohol, with an aqueous solution of a hydroxide of tetra-alkylammonium having the formula (I):

$$R'_4N\text{-}OH$$

wherein R′ represents a C_3-C_7 alkyl group and of one or more soluble or hydrolizable compounds of one or more metals selected from Ti, V, Zr, Sn, the quantity of the constituents of the above solution being such as to respect the following molar ratios:

alcohol/YO = 5-20

R'_4N-OH/YO = 0.05-0.5;

H_2O/YO = 5-30

YO/MO $\geq$ 5

whereas the ratio $H2O/R'_4N^+$ varies according to the number of carbon atoms in the R′ alkyl chain , in accordance with the values shown in table A below :

Table A

R′	H_2O/R'_4N+
Hexyl	> 133
Pentyl	> 100
Butyl	> 73
Propyl	> 53

operating at a temperature close to the boiling point, at atmospheric pressure, of the alcohol used and of any alcohol which develops as by-product of the above hydrolysis reaction, without the elimination or substantial elimination of said alcohols from the

reaction environment, preferably at a temperature of between 20°C and 80°C;

(b) subjecting the gel obtained in step (a) to drying;

(c) outgassing the obtained material in vacuum and then adding a solution of silylating agent in solvent under inert gas;

(d) refluxing the resulting mixture under inert atmosphere and then filtering the obtained product, washing and subjecting it to drying.

45) Process for preparing the catalytic composition of claim 42, comprising a completely amorphous micro-mesoporous mixed oxide containing a matrix selected from silica, alumina, ceria, magnesia and mixtures of thereof (YO), wherein one or more metal oxides (MO) selected from transition metal oxides and group IVA metal oxides are uniformly dispersed, whose surface has $-O-Si(R)_3$ groups, R being the same or different each other and being selected from C_1-C_4 alkyl, aryl and polyaryl groups, that optionally contain functional groups selected from acids, amines, thiols, sulfonics or trialkylamines, characterized by a surface area of more than 500 m^2/g, a pore volume of between 0.3 and 1.3 ml/g, an average pore diameter of less than 40 Å,

whose XRD spectrum from powders does not have a crystalline structure, does not show any peak and shows a widespread scattering at angular value not greater than $2\theta = 5°$, with CuKα radiation, while other scattering phenomena coherent for greater angular values are absent, said process comprising :

(a) subjecting to hydrolysis and gelification a solution of one or more soluble or hydrolizable compounds of Si, Al, Ce, Mg, or mixture thereof, in alcohol, with an aqueous solution of a hydroxide of tetra-alkylammonium having the formula (I):

$$R'_4N\text{-}OH$$

wherein R' represents a C_3-C_7 alkyl group and of one or more soluble or hydrolizable compounds of one or more metals selected from Ti, V, Zr, Sn, the quantity of the constituents of the above solution being such as to respect the following molar ratios:

alcohol/YO = 5-20

R'_4N-OH/YO = 0.05-0.5;

H_2O/YO = 5-30

YO/MO $\geq$ 5

whereas the ratio $H2O/R'_4N^+$ varies according to the number of carbon atoms in the R' alkyl chain , in

accordance with the values shown in table B below :

Table B

R'	H_2O/R'_4N^+
Hexyl	$\leq$ 133
Pentyl	$\leq$ 100
Butyl	$\leq$ 73
Propyl	$\leq$ 53

operating at a temperature close to the boiling point, at atmospheric pressure, of the alcohol used and of any alcohol which develops as by-product of the above hydrolysis reaction, without the elimination or substantial elimination of said alcohols from the reaction environment, preferably at a temperature of between 20°C and 80°C;

(b) subjecting the gel obtained in step (a) to drying;

(c) the obtained material is outgassed in vacuum and then a solution of silylating agent in solvent;

(d) refluxing the resulting mixture under inert atmosphere and then filtering the obtained product, washing and subjecting it to drying.

46) Process for preparing the catalytic composition of claim 45 comprising :

(a) subjecting to hydrolysis and gelification a solution of one or more soluble or hydrolizable compounds of Si and Al, in alcohol, with an aqueous solution of a hydroxide of tetra-alkylammonium having the formula (I):

$$R'_4N\text{-}OH$$

wherein R' represents a C_3-C_7 alkyl group and of one or more soluble or hydrolizable compounds of one or more metals selected from Ti, V, Zr, Sn, the quantity of the constituents of the above solution being such as to respect the following molar ratios:

alcohol/YO = 5-20

R'_4N-OH/YO = 0.05-0.5;

H_2O/YO = 5-30

YO/MO $\geq$ 5

whereas the ratio $H2O/R'_4N^+$ varies according to the number of carbon atoms in the R' alkyl chain , in accordance with the values shown in table B below :

Table B

R'	H_2O/R'_4N^+
Hexyl	$\leq$ 133
Pentyl	$\leq$ 100
Butyl	$\leq$ 73
Propyl	$\leq$ 53

operating at a temperature close to the boiling point, at atmospheric pressure, of the alcohol used and of any alcohol which develops as by-product of the above hydrolysis reaction, without the elimination or substantial elimination of said alcohols from the reaction environment, preferably at a temperature of between 20°C and 80°C;

(b) subjecting the gel obtained in step (a) to drying;

(c) the obtained material is outgassed in vacuum and then a solution of silylating agent in solvent was added under inert gas;

(d) refluxing the resulting mixture under inert atmosphere and then filtering the obtained product, washing and subjecting it to drying.

47) Process according to claim 43 or 45 wherein the silylating agent is hexaalkyldisilazane or hesaaryldisilazane wherein the alkyl or aryl groups of the disilazane are selected from C_1-C_4 alkyl, phenyl and polyaryl groups, that optionally contain functional groups selected from acids, amines, thiols, sulfonics or trialkylamines.

48) Process for preparing a micro-mesoporous completely amorphous mixed oxide of MSA type containing a matrix of an oxide (YO) selected from silica, alumina, ceria, magnesia and mixtures of thereof, wherein one or more metal oxides (MO) selected from transition metal oxides and group IVA metal oxides are uniformly dispersed, comprising:

(a) subjecting to hydrolysis and gelification a solution of one or more soluble or hydrolizable compounds of Si, Al, Ce, Mg, or mixture thereof, in alcohol, with an aqueous solution of a hydroxide of tetra-alkylammonium having the formula (I):

$$R'_4N\text{-}OH$$

wherein R′ represents a C_3-C_7 alkyl group and of one or more soluble or hydrolizable compounds of one or more transition metals or group IVA metal, preferably selected from Ti, V, Zr, Sn, the quantity of the constituents of the above solution being such as to respect the following molar ratios:

alcohol/YO = 5-20

R'_4N-OH/YO = 0.05-0.5;

H_2O/YO = 5-30

$YO/MO \geq 5$

whereas the ratio H_2O/R'_4N^+ varies according to the number of carbon atoms in the R' alkyl chain , in accordance with the values shown in table A below :

Table A

R'	H_2O/R'_4N+
Hexyl	> 133
Pentyl	> 100
Butyl	> 73
Propyl	> 53

operating at a temperature between the room temperature and the boiling point, at atmospheric pressure, of the alcohol used and of any alcohol which develops as by-product of the above hydrolysis reaction, without the elimination or substantial elimination of said alcohols from the reaction environment, preferably at a temperature of between 20°C and 80°C;

(b) subjecting the gel obtained in step (a) to drying and calcinations.

49) Process according to claim 43, 45 o 48 where the mixed oxide contains silica and alumina and in the step (a) a soluble or hydrolizable compound of Si and a

soluble or hydrolizable compound of Al are used, in the molar ratio $SiO_2/Al_2O_3 \geq 30$.